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AN ELECTRODE FOR A BATTERY AND A SECONDARY BATTERY
[電池用電極及び二次電池]

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SPECIFICATION

1. Title of the Invention

An Electrode for a Battery and a Secondary Battery

2. Scope of Patent Claims

1. An electrode for a battery, comprising a layer of porous non-conductive material, which is formed on the surface of a conductive base.

2. The electrode according to Claim 1, wherein the layer of porous non-conductive material is a layer of porous ceramics.

3. The electrode according to Claim 1, wherein the layer of porous non-conductive material is a sintered body layer of ceramics particles.

4. The electrode according to Claim 1, wherein the conductive base is aluminum metal and the layer of porous non-conductive material is a layer of alumina.

5. A secondary battery, comprising an electrode consisting of a layer of porous non-conductive material formed on the surface of a conductive base and an opposite pole, which are soaked in an electrolytic solution.

6. The secondary battery according to Claim 5, wherein the opposite pole is any of a carbon electrode,

titanium disulfide, an iron sulfide electrode, and a vanadium pentoxide electrode.

3. Detailed Description of the Invention

The present invention relates to an electrode for a battery and to a secondary battery using this electrode. In further detail, it relates to an electrode for a battery that conducts an electrochemical reaction by using spaces on a layer of a porous non-conductive material formed on the surface of the electrode, and to a secondary battery composed of this electrode, an opposite pole, and an electrolytic solution.

In recent years, accompanied by the development and multi-functionization of electronics-related

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equipment, demand for a high performance battery has been increased. Particularly, a lithium battery has gained attention due to its characteristics, that is, high output and high energy density, and studies have been conducted to overcome the high cost caused by the use of lithium by making the battery a secondary battery. However, a large difficulty of forming a so-called dendrite, that is, the deterioration of the lithium electrode itself due to repeated charging and discharging, has hindered the

achievement of studies for making lithium a secondary battery. In addition, recently, the development of a lithium secondary battery that resists producing a dendrite by having a wood metal occlude lithium has been reported. However, since wood metal itself is an alloy of several kinds of heavy metals, high energy density, which is an important characteristic of a lithium battery, is sacrificed.

Under the actual conditions such as these, the present inventors have conducted studies in order to obtain a secondary battery that has the characteristics of high output and high energy density and that does not form any dendrite, especially paying attention to the electrodes. As a result, we found that if a layer of porous material was formed on the surface of the electrode and an electrochemical reaction was conducted by using spaces on the layer, then a secondary battery that satisfied the above mentioned demand could be obtained. Thus, we completed the present invention.

In other words, the present invention is to provide an electrode for battery comprising a layer of porous non-conductive material formed on the surface of a conductive base, and a secondary battery comprising this electrode and an opposite pole, which are soaked in an electrolytic

solution.

The electrode of the present invention is prepared by treating the surface of a conductive base to make a layer of porous non-conductive material or by putting a conductive base and a porous material membrane together. As the conductive base, any material having conductivity, such as metal, carbon material, or a conductive high molecular compound, can be used. In addition, the examples of the porous non-conductive material to be used in the present invention include all materials that have electrical insulation properties and are porous or applicable for a porosifying process, such as glass, ceramics, and organic polymer film. To porosify the surface of the electrode and the like, surface porosifying techniques that are presently commonly conducted, such as sintering particles, chemical erosion, electrolytic oxidation, and ion spattering, can be used. The size of the hole is 10 Å to 1 mm or desirably 100 Å to 10 µm. In addition, a conductive base and a porous non-conductive material membrane are put together using a technique such as vapor deposition of metal, impregnation of fused metal, and ion plantation. Of the electrodes prepared in these ways, those made of alumina, organic film, and the like are desirable from the perspective of weight reduction of the battery itself. Especially, those

made of aluminum metal foil (plate), which are anodized by a usual method and have their surface altered to porous alumina membranes, are desirable. Incidentally, for the electrode of the present invention, a conductive base, in principle, needs to be exposed at the bottom of hole.

However, it is permissible if there is a non-conductive thin membrane such as an alumina layer with a thickness of 30 Å or less, which just shows electronic conductivity substantially.

Additionally, to compose the secondary battery of the present invention, the above mentioned electrode and an opposite pole are in an electrolytic solution. As the opposite pole, an electrode that is chargeable and dischargeable, such as a carbon electrode, titanium disulfide electrode, iron sulfide electrode, and vanadium pentoxide electrode, is used. In addition, the

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electrolytic solution is prepared by dissolving an electrolyte in a solvent. Anything known as the electrode active material of an electrolyte can be used. Desirable examples are metals, including alkali metals, zinc, and lead. Especially, metals that can easily form dendrite, such as lithium and zinc, are desirable. In addition, examples of the electrolytic counter ion include a

perchloric acid ion, phosphorous hexafluoride ion, thallium hexafluoride ion, arsenic hexafluoride ion, antimony hexafluoride ion, halogen ion, nitric acid ion, sulfuric acid ion, and rhenium tetroxide ion. In addition, examples of the solvent include a general solvent for an organic battery, such as propylene carbonate, γ -butyrolactone, dimethoxy ethane, THF, dioxane, and acetonitril.

Fig. 1 shows one example of compositions of the secondary battery of the present invention. That is, an electrode 2 and an opposite pole 4 of the present invention are facing each other across a separator 3. These electrodes are soaked in an electrolytic solution and are confined tightly.

When charge is conducted using the secondary battery as in the above mentioned present invention, an electrode active material is precipitated at only the bottoms of the holes of the electrode of the present invention (near a conductive base), filling spaces from the bottom part consecutively. Accordingly, as long as charge and discharge are repeated in a range in which metal is precipitated in these spaces, the formation of dendrite due to the concentration of electric current to the tip part can be prevented, and, in addition, a decrease in the charge/discharge efficiency due to the lack of active

material precipitated can be restrained. Thus, a battery using the electrode of the present invention realizes a high output and high energy density and does not form dendrite in practical use.

The present invention is described below referring to examples.

Example 1.

A high-purity aluminum metal (99.99 %; thickness: 100 μm) was anodized in 0.4 M phosphoric acid (30 mA/cm²; 140 V; 18 minutes) to form 10 μm of porous alumina layer on the surface. This electrode (1 x 2 cm) and active carbon fiber (CH-20 manufactured by Kuraray Chemical Co., Ltd.; 2 x 2 cm) as an opposite pole were used to compose a battery with 1.0 M LiBF₄ propylene carbonate as an electrolytic solution. Constant current charge/discharge characteristics (for 30 minutes; 300 μA charged) of this battery were as is shown in Fig. 2, and stable electric potentials by the charge/discharge of lithium were observed. This battery was dismantled after the charge/discharge to observe spaces on the alumina electrode, and the lithium metal disposed homogeneously in these spaces. Thus, it was confirmed that the lithium metal was precipitated in the spaces of alumina as expected.

Example 2.

A high-purity aluminum metal (99.99 %; thickness: 300 μm) was anodized in 14 % by weight of sulfuric acid (30 mA/cm²; 50 V; 30 minutes) to form 20 μm of porous alumina layer on the surface. This electrode (1 x 2 cm) and active carbon fiber (CH-15 manufactured by Kuraray Chemical Co., Ltd.; 2 x 2 cm) as an opposite pole were used to compose a battery with 0.5 M LiClO₄ propylene carbonate as an electrolytic solution. The constant current charge/discharge characteristics of this battery were as is

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shown in Fig. 3.

Example 3.

Aluminum was coated by melt injection on one side of a setter for an unglazed ceramics condenser (ZIRON-HS manufactured by Nippon Sheet Glass, Co., Ltd.) to make an electrode. This electrode and active carbon fiber (CH-20; 2 x 2 cm) as an opposite pole were used to compose a battery with 1.0 M LiBF₄ propylene carbonate as an electrolytic solution. The constant current charge/discharge characteristics of this battery were as is shown in Fig. 4.

4. Brief Description of the Drawings

Fig. 1 is a drawing that shows one example of the compositions of the secondary battery of the present invention.

Fig. 2 is a drawing that shows the relationship between the time when charge/discharge was conducted at the constant current (300 μ A) and the voltage between both electrodes.

Fig. 3 is a drawing that shows the relationship between the time when charge/discharge was repeated at the constant current (100 μ A) and the voltage between both electrodes.

Fig. 4 is a drawing that shows the relationship between the time when charge/discharge was conducted at the constant current (500 μ A) and the voltage between both electrodes.

- 1: a platinum lead wire
- 2: an electrode as the present invention
- 3: a separator
- 4: an opposite pole
- 5: a clip
- 6: a Teflon plate
- 7: a Teflon volt
- 8: a Teflon nut

Fig. 1

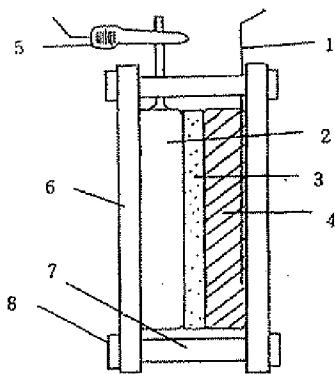


Fig. 2

Constant current charge/discharge characteristics; 300 μ A

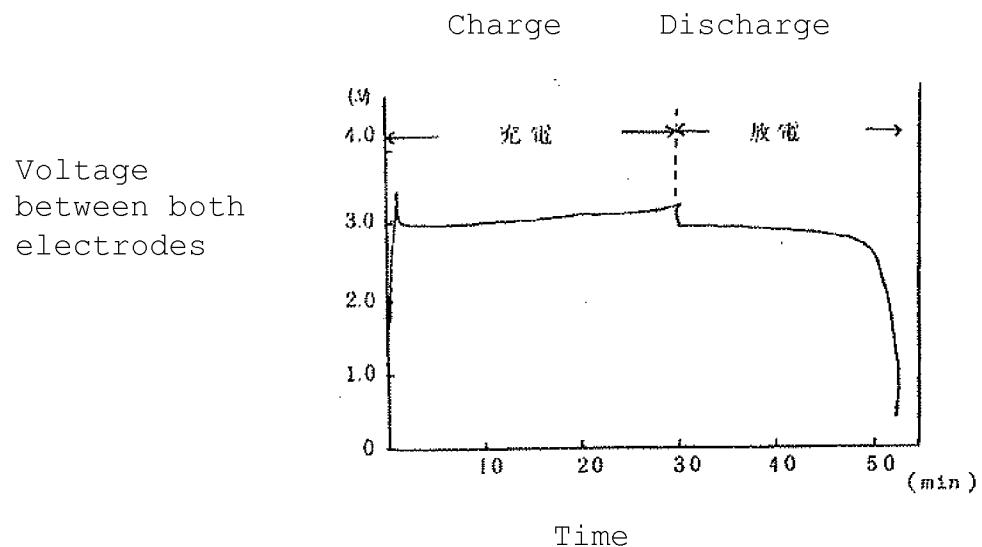
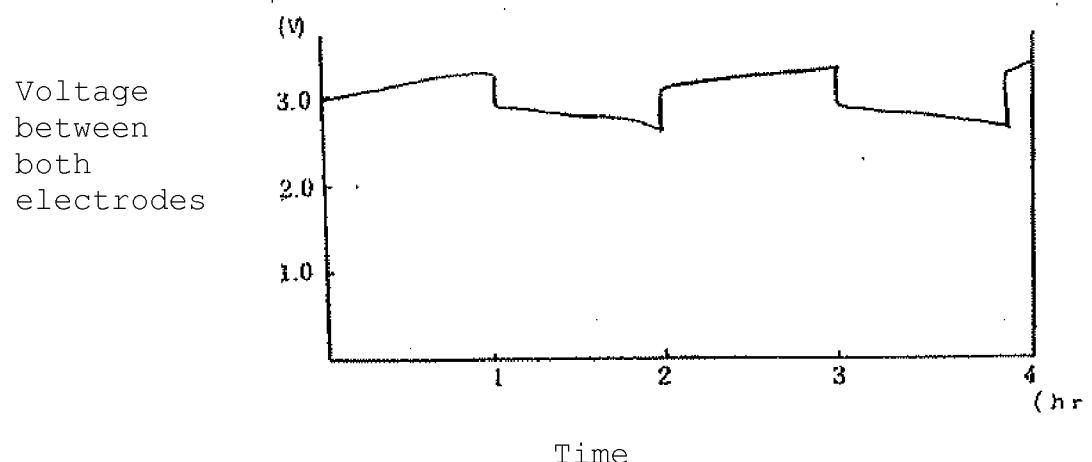


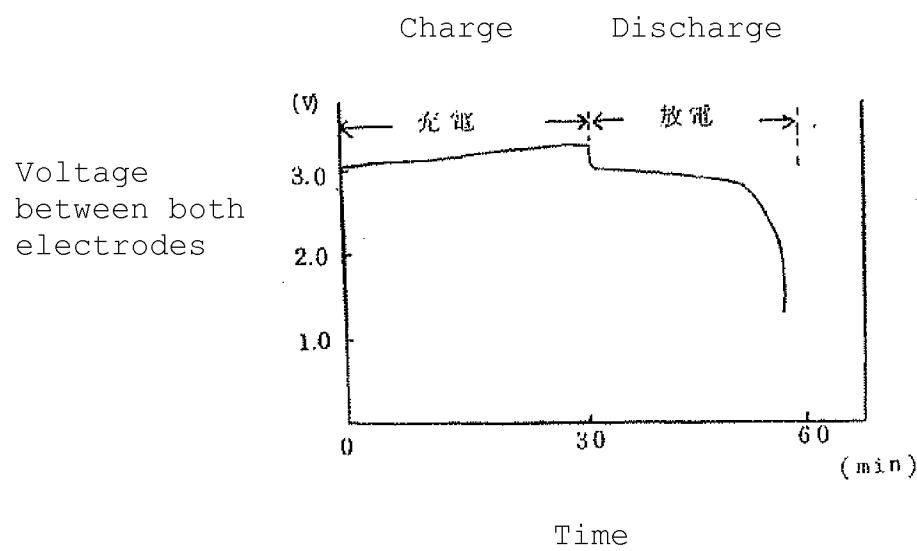
Fig. 3



Time

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Fig. 4



Time